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CEMENT-BASED MATERIALS FOR USE IN THE DISPOSAL OF LOW-LEVEL AND MEDIUM-LEVEL RADIOACTIVE WASTES
LITERATURE REVIEW

Report No. 87-108-K

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ABSTRACT

This report contains the findings of a literature review on the use of cement-based materials in the disposal of low- and medium-level radioactive waste. The desirable performance characteristics of these materials are outlined. The effect of various mix components on the mechanical, hydraulic, chemical, thermal and emplacement properties is discussed. Information on cement-based materials both from within Ontario Hydro and from external sources has been reviewed. A small number of basic mix components are recommended for study in the development of a grout for low- and medium-level radioactive waste storage.

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EXECUTIVE SUMMARY

CEMENT BASED MATERIALS FOR USE IN THE DISPOSAL OF LOW-LEVEL AND MEDIUM-LEVEL RADIOACTIVE WASTES

J.J. Deans/H.M. Andre

This report details the findings of a literature review on the use of cement-based materials for various applications in the disposal of low- and medium-level radioactive wastes. Cement-based materials show promise for use in this area of application. They can be designed to have the desired performance characteristics, yet the material components are economical, readily available, and easily placed.

In the process of examining the use of cementitious materials, the following items were considered:

1. The desirable performance characteristics, or properties, of these materials.
2. The effect of the various mix components on the properties.
3. A review of the cement-based materials that have been studied previously.

The desirable performance characteristics discussed are those related to the mechanical, hydraulic, chemical, and thermal properties, as well as the emplacement requirements. The mix components studied include: (a) cements (ie, normal portland, sulphate resistant portland, shrinkage compensating); (b) pozzolanic additives (ie, fly ash, silica fume, natural pozzolans); (c) non-pozzolanic additives (ie, aggregates, clays); and (d) chemical admixtures (ie, superplasticizers, expanding agents, set retarders). The advantages and disadvantages of using each of these mix components are discussed, and tables are included which detail the individual references reviewed.

The specific cement-based materials found in the literature are grouts and bulk backfill materials. Although some of the mixes discussed are not directly applicable to the disposal of low- and medium-level wastes, each mix contributes towards gaining a better understanding of the effect of the mix components on the material properties. Among the grouts discussed are those developed in the United States in connection with low- and high-level radioactive waste disposal, as well as a variety of grouts developed at Ontario Hydro.

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Some of the findings are that the influence of the individual mix components on grout properties is reasonably well understood, and that site-specific characteristics must be established in order that future materials research can proceed along a narrower field of study. Grouts that are non-shrinking or expansive to some degree have been identified as the most suitable for use in radioactive waste disposal systems.

Further research is required on the longevity, the chemical stability, the thermal expansion and contraction characteristics, the effect of shrinkage due to the heat of hydration, and the problems associated with emplacement techniques (ie, pumpability and quality control). The primary requirement for achieving a durable grout is that low water/solids ratios be used in order to attain adequate strength and reduce the porosity and permeability. Other factors which are important for achieving a durable grout are the use of properly graded aggregates, supplementary cementing materials (ie, fly ash, slag) and admixtures (ie, superplasticizers).

Based on this literature review, a small number of basic mix components are recommended for study in the development of a grout for low- and medium-level radioactive waste storage applications. Experimental work is required in order to obtain relevant information on the durability/stability of grouts.

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CEMENT-BASED MATERIALS FOR USE IN THE DISPOSAL OF LOW-LEVEL AND MEDIUM-LEVEL RADIOACTIVE WASTES
LITERATURE REVIEW

J.J. Deans/H.M. Andre

1.0 INTRODUCTION

This report focuses on the use of cement-based materials (ie, grouts) in low- and medium-level radioactive waste (LLW and MLW) disposal. Laboratory studies of proposed mix formulations and actual mixes used in the field have been reviewed. This includes both in-house and external information. Various types of cement, additives, aggregates and chemical admixtures have been used. The effect of these components on the physical characteristics of the grout must be well understood in order to develop specially tailored mixes for the particular disposal scheme.

1.1 Report Organization

Sections 2.0 through 5.0 contain the principal findings from the literature reviewed. Specific information regarding the mix proportions and the physical and chemical characteristics of the materials is contained in the appendices.

All references cited have been subdivided into work done externally and within Ontario Hydro (ie, Prefix H refers to internal Hydro work).

The mechanical, hydraulic, chemical, thermal, and emplacement requirements for the cementitious materials considered are outlined in Section 2.0. Depending on the disposal scheme, some or all of these requirements will play an important role.

The various materials used in the development of grouts are outlined in Section 3.0. Among the mix components discussed are: (a) cements (ie, portland, sulphate resistant); (b) pozzolanic additives (ie, fly ash, silica fume, natural pozzolans); (c) non-pozzolanic additives (ie, aggregates, clays); (d) chemical admixtures (ie, superplasticizers, expanding agents, set retarders).

The development of specific grouts considered for application in radioactive waste disposal systems is outlined in Section 4.0. Section 5.0 discusses materials developed for use as bulk backfill, consisting mainly of sand-cement mixtures with a large proportion of sand.

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Due to the large amount of data reviewed, only general comments on the mix proportions and a brief review of the performance characteristics for the various mixes can be made. Specific details on mix proportions and performance characteristics are given in the accompanying Appendices A, B, and C, which correspond to Sections 3.0, 4.0, and 5.0.

1.2 Previous Work Summary

Many detailed studies on grouts for use in radioactive waste disposal have been carried out/1,2,3,4,5,6/. In 1979, the Canadian Centre for Mineral and Energy Technology (CANMET) issued a report covering both the materials development and the placement requirements for grouts used in radioactive waste disposal/5/. In 1984, the Civil Research Department of Ontario Hydro issued a report detailing the performance requirements of cementitious materials for use in borehole plugging/H-1/. Even though these reports deal mainly with the disposal of high-level waste, the information on cement-based materials is applicable to the LLW and MLW program.

2.0 ENGINEERING PROPERTIES

All cement-based materials developed for use in radioactive waste disposal systems will be required to do at least one or more of the following:

- inhibit fluid flow
- inhibit radionuclide migration
- provide structural integrity

Compliance with these requirements will be determined from examination of the material behaviour characteristics, which can be broadly divided into five categories (mechanical, hydraulic, chemical, thermal, and emplacement). Table I identifies the engineering properties which will be discussed in the following sections. Table II outlines some of the tentative design requirements for the grout and concrete mixes.

2.1 Mechanical Properties

2.1.1 Compressive Strength

Sufficient strength is required to withstand the stresses imposed on the material both during and after disposal. These stresses may be induced by mechanical loading, temperature, and overburden or uplift pressures. Required strength will depend largely on the intended application of the cementitious material. For borehole sealing, a recommended range for the grout and concrete strength is 25-50 MPa /3,4,7/. Grouts can be designed to have compressive strengths of up to 100 MPa with the use of fly ash or silica fume, and superplasticizers.

2.1.2 Bond

A good contact between the host medium and the cementitious material is necessary to limit the permeability of the system, and prevent differential movement of the material under stress. In basalt, a bond strength of 10 MPa

was obtained for clean rock and 2.5 MPa for mud-contaminated rock/8/. In anhydrite, bond strengths ranging from 2.6 to 7.4 MPa were achieved at 28 days, depending on the grout formulation used/9/.

When simulated borehole specimens are used to determine bond strength or permeability, great care must be taken to avoid cracking or separation at the interface during curing/9,10,11,12/. This has been accomplished by keeping specimens wet at all times, as well as maintaining some confining pressure on the specimens to prevent stress-relief cracking/9/.

2.1.3 Expansion/Shrinkage

It is generally recognized that one method of improving the bond between the grout and the host medium is to use a grout having expansive properties. In many cases this expansion has been achieved with the use of expansive or shrinkage compensating cements or with expansive additives. The expansion should preferably occur after setting and should be enough to maintain contact with the boundary but not so high as to induce undesirable stresses.

The expansion characteristics of various grout mixtures have been studied at Sandia National Laboratories, the Waterways Experiment Station (WES) and Pennsylvania State University (PSU); however, to date no optimum expansion limits have been set. Test methods for determining expansion have been outlined/8/, and generally, the amount of expansion has been determined from both unrestrained and restrained prisms (ASTM C806-75)/4,9,11,13,14,15/. Care must be taken in determining the amount of expansion because the effects of temperature and storage conditions have been shown to significantly alter the results/4,9,10/. The various expansion mechanisms related to grouts developed in the U.S. are discussed in some detail in Sections 4.1 and 4.2.

Many factors can influence shrinkage; for example, neat cement grouts have been shown to shrink significantly more when water-cement ratios rise above 0.5/H-2/.

2.1.4 Ductility/Elasticity

The grout and the host rock should have similar elastic and deformation characteristics to produce a compatible system/1,16,17/. The grout should have sufficient deformability to allow for rock or soil movement without the development of cracks, this being particularly important in seismic zones. A tentative requirement for the minimum modulus of elasticity for grouts is 13.8 GPa/7/ and that for concrete is 45 GPa/4/.

2.1.5 Longevity

The effect of in-situ conditions on the mechanical properties of the grouts over the long term is of concern. Work in this area is not extensive and it has been identified as a primary area for future research/18/. Grout formulations developed in the late 1970's in the laboratories and used in the field continue to be monitored, and recent 4 and 5 year durability studies have been published/2,3,19/. A study of a sample of 17 year old grout used in rock/20/ showed the contact surface between the grout and the rock wall was tight, and there was no evidence of deterioration of the grout. The excellent

durability of some 4 year, 17 year and 19 year old air-entrained fly ash concrete under various exposure conditions has also been reported by Ontario Hydro/H-3,H-4/. Gyenge studied the longevity of grouting materials using numerical models which consider the physical stability of a grout based on chemical erosion over time, and the action of the natural hydrogeological environment; however, specific site characteristics as well as specific mix properties would need to be considered in a final assessment/21/.

2.2 Hydraulic Properties

2.2.1 Permeability

One of the primary purposes of a cement-based backfill material used in a radioactive waste disposal scheme is to inhibit fluid flow; therefore, the permeability of the material is extremely important. Permeability is an index of the rate at which water can flow through a material, or through any interface of the material with the host medium. The grout itself and the interface between the grout and rock should have a low permeability to both liquids and gases/13/. However, the permeability of the grout need not be lower than that of the host medium/22/. The maximum allowable permeability of grouts for use in underground borehole and shaft sealing has been given as 10^{-12} m/s at three months/7,21/, while for concrete the maximum permeability has been quoted as 10^{-11} m/s/4/. Other information dealing with borehole plugging considers a sufficiently dense medium as one whose permeability is in the range of 10^{-12} to 10^{-13} m/s/23/. The permeability of the waste storage system as a whole must also be considered, in which case the permeability of the grout material-host medium interface should be examined/10,12,23,24,25/. McDaniel achieved some success in relating liquid permeabilities to the more easily measured air permeabilities/12/, although air permeabilities have been shown to be significantly higher than water permeabilities/26/.

2.3 Chemical Properties

2.3.1 Leachability

Leachability is a measure of the resistance of a cement-based material to various forms of chemical attack. A low leach rate is required to reduce the possibility of radionuclide migration and to reduce the detrimental changes that can occur in the grout or backfill through leaching/21/. Leach tests can either measure the leach rate of the chemical compounds which make up a hardened cementitious material or that of radionuclide tracers (such as Strontium-85, Cesium-137, and Cobalt-60)/6/.

2.3.2 Sorptivity

Sorptivity is a measure of the ability of a grout or backfill material to retard radionuclide movement by some means of fixation, such as absorption, adsorption, or chemical bonding. The sorption ability of a seal material would create an additional barrier to reduce the rate of release of radionuclides into the biosphere/21,27/. Sorptivity can be enhanced with the addition of certain natural pozzolanic materials and mineral admixtures such as clays/6,28,29,30/. The sorption of strontium (Sr), cesium (Cs), nickel (Ni), iodine (I) and carbon (C) in concrete has been studied in Finland/27/.

This study found that the relative sorption capacity was Ni>C>Cs>I>Sr. As well, it was observed from autoradiograms that the sorption of cesium and carbon occurred mainly in the sand fraction, and the sorption of iodine mainly in the cement paste. The order of the penetration depths of the radionuclides into the concrete was found to be Sr>I>C>Cs.

2.3.3 Stability/Longevity

The host medium, cementitious filler and ground water should be a chemically-stable system. Reactions, which may occur during the design life of the material, must not cause detrimental changes to its functions. To determine possible chemical reactions, an investigation of the material using mineralogical and morphological determination by x-ray diffraction (XRD), scanning electron microscope (SEM) or optical microscope techniques will be required/31/. One factor which may affect the chemical stability of the material is the presence of sulphate, hydrogen, chloride, and other aggressive ions in the ground water/13/. This consideration would obviously be very site specific since the ground water composition changes for the various locations. For instance, in the Canadian high-level waste research program, a standard Canadian Shield brine solution was developed for use in leach tests/48/. The influence of the process of weathering must also receive consideration, especially for near surface storage.

2.4 Thermal Properties

2.4.1 Thermal Expansion/Contraction

A coefficient of thermal expansion similar to that of the host medium will reduce differential responses to temperature, thereby reducing the potential for cracking/16,21,32/. Expansion/contraction behaviour due to ambient temperature fluctuations in above ground storage systems is also very important. Thermal coefficient of expansion values for hydrated portland cement paste range between 11 x 10^{-6} and 16 x 10^{-6} m/m/°C, while for sanded grouts the thermal expansion is generally lower with values in the order of 5 x 10^{-6} m/m/°C/33/. No numerical requirements have been established since this is a site-specific characteristic.

2.4.2 Thermal Conductivity or Diffusivity

Thermal conductivity or diffusivity is important for determining thermal gradients and thermally induced stresses which may develop in cementitious materials. The thermal conductivity value can be adjusted by the addition or substitution of pozzolanic materials, aggregates, or chemical admixtures.

2.4.3 Heat of Hydration

The heat of hydration of cement grouts should also be considered since it will result in a temperature rise at early ages and thermal shrinkage cracking can result upon subsequent cooling. The shrinkage cracks may lead to an increase in permeability of the grout. This problem is of particular concern if the grout is to be used as a bulk backfill material because a large volume of grout can generate a lot of heat during hydration.

2.5 Emplacement Properties

2.5.1 Working Time

The working time must be of sufficient length to ensure that setting does not occur during transportation and placement/2/. The actual time required will depend on the final design for the storage system. Soon after placement, the material should set so that the possibility of external contamination will be minimized. A 2 to 3 hour working time was the requirement for work completed at the U.S. Army Engineers (USAE) Waterways Experiment Station (WES)/13/.

2.5.2 Bleeding and Segregation

Bleeding and segregation both involve the separation of the mixing water from the newly placed grout due to settlement of the solids within the mass. This problem must be minimized in order to reduce strength variations and the formation of weaker zones at the surface of a material due to the presence of bleed water. No bleeding limits are suggested in the literature, and for many of the cementitious mixes under consideration this is not a significant problem since low water/cementing materials ratios are used.

2.5.3 Fluidity/Pumpability

The criteria for pumpability is highly dependent on such site-specific factors as the grouting equipment available, and the transport time required. Grouts developed for use in underground disposal schemes were required to have a flow cone value of 18 seconds or less (CAN/CSA A23.2).

2.5.4 Feasibility of Emplacement

The choice of the emplacement method will depend on the disposal system. Grout pumping techniques and bulk backfill placement methods are included in a 1979 ONWI report/1/ and a 1979 CANMET report/5/. Information on the technical and practical application problems can also be collected from actual field uses of cementitious materials, and therefore these reports are quite valuable sources of information/34,35,H-5/.

2.5.5 Effect of Emplacement on Seal Properties

The effect of the emplacement method on the sealing properties of the grout should be well understood. Cores taken from grouts used in the field to fill test boreholes indicate no significant problem with in-place seal properties/2,6,9,26,29,36/. However, site trials should be performed to identify any potential problems.

2.5.6 Quality Control

Since many of the grout formulations developed contain a large number of components, strict quality control will have to be maintained to ensure that a consistent composition with satisfactory properties is attained. In order to minimize potential problems, the grout formulations should contain as few ingredients as possible.

3.0 MIX COMPONENTS

Cement-based materials can contain a variety of ingredients. These include different cement types (ie, normal portland, sulphate resistant portland, masonry), supplementary cementing materials (ie, natural pozzolans, fly ash, silica fume, slag), admixtures (ie, water reducers, set retarders, expanding agents) and aggregates (sand and stone).

3.1 Cements

Table III identifies the different types of cements studied.

3.1.1 Portland Cement

According to CAN/CSA A5 specification, portland cements consist of five types: Type 10 (Normal), Type 20 (Modified), Type 30 (High Early Strength), Type 40 (Low Heat), and Type 50 (Sulphate Resistant). Typical chemical compositions for these cements available in Ontario are given in Table A1 (Appendix A). Each type is designed to provide specific properties during the early stages of hydration. For most of the cement types, the ultimate strengths are the same, although those which have a slow rate of strength gain (Types 40 and 50) generally tend to have a higher ultimate strength. Type 30 is a more finely ground cement having a high C_3S (tricalcium silicate) content. This results in a rapid hardening cement with a high heat evolution and a lower ultimate strength. Type 50 cement has a low C_3A (tricalcium aluminate) content (<3.5%) which makes it sulphate resistant. Other types of cements are also available as shown in Table A2 (Appendix A).

Various portland cement types were used in some of the early grout formulation work at WES for the borehole plugging program/13/; however, only Type 30 cement was chosen for further study/14,37/. In connection with low-level and medium-level radioactive waste solidification, Portland Types 10, 20, and 30 have been used/6,28,38,39,40/.

3.1.2 Aluminous Cement

A typical chemical composition of aluminous cement is given in Table A2 (Appendix A). Aluminous cement is resistant to chemical attack by sulphates, CO_2 dissolved in pure water, and some dilute acids (pH greater than 3.5 to 4) with the exception of hydrochloric, hydrofluoric or nitric acid /H-6/. The resistance to sulphate attack is due to the absence of any hydrated lime in the hardened paste, and also due to the protective influence of the relatively inert alumina gel formed during hydration. High alumina cement will develop high early strength, but this high strength may deteriorate with age due to the conversion of metastable hexagonal hydrates to stable cubic products in the cement matrix/H-6/. This conversion is accelerated under high temperature and moist conditions/41,42/. High alumina cement can also be used as an additive to ordinary cement to act as a set accelerator; however, less than 20 percent replacement should be used to avoid flash setting/33/.

3.1.3 Oil Well Cements

Oil well cements are a group of specialized cements used by the oil and gas industry to seal exploration wells and dried-up wells. These cements are often subjected to high temperature and pressure, as well as corrosive conditions. It is the sulphate resistance of some of the oil well cements that has attracted the attention of researchers in the underground disposal of radioactive wastes. The three types of oil well cements reviewed are classified by the American Petroleum Industry (API) as Class C, Class G and Class H.

Class C is a high early strength cement available in sulphate resistant (SR) or highly sulphate resistant (HSR) types. Its early strength characteristics make it similar to portland Type 30 cement; however, Class C cement has a much lower C_3A content. In some of the work reviewed, Class C cements with no C_3A were used/14,37/. Class H cement is similar to Type 50 portland cement except that it is ground coarser, has no fineness requirement, and the C_3A content is limited to a maximum of 3%/43/. This cement is available only in moderate sulphate resistance, but Class G oil well cement, which is very similar to Class H, and can also meet CAN/CSA A5 Type 50 requirements, is available in moderate to high sulphate resistance/44/. A typical chemical composition for Class G oil well cement is given in Table A2 (Appendix A). A study of the relative leaching resistance of grouts made with normal portland cement and Class G oil well cement found that the sulphate resistant Class G cement improves the leaching resistance significantly/H-7/.

3.1.4 Type K (Expansion/Shrinkage Compensating) Cements

According to ASTM, Type K is an expanding and/or shrinkage compensating cement (see Table A2, Appendix A, for chemical composition). An expansive cement is one which when mixed with water forms a paste that increases in volume after setting/26/. The volume increase is due to the formation of ettringite, which is a product of the reaction of gypsum with C_3A/4,26/. Most of the expansive cements are also sulphate resistant/13,14,37/. Long-term (4 yr and 5 yr) durability studies of grouts formulated using these cements, both in the laboratory and in the field, have recently been published/2,3,19/, and the results indicate good durability.

Expanding or non-shrinking cements are especially suited for sealing applications because they improve the bond and have been shown to decrease the permeability of the grout/14/.

The expansive behaviour of most cements can be enhanced with the addition of proper expanding admixtures (see Section 3.3.3).

3.1.5 Masonry Cement

Masonry cement is a blend of portland cement and lime. The lime can be in the form of ground limestone ($CaCO_3$) or in the form of slaked lime ($Ca(OH)_2$)/39/. Masonry cement has a high plasticity and is capable of developing strong bonds; however, its compressive strength is not as high as portland cements/6/. Masonry cement exhibits high water retention values that make it well suited for the solidification of LLW waste streams/6/. Masonry cement

can incorporate higher waste loadings than portland cements and its bulk density is about 35 percent less than that of portland cement/39/. Masonry cement has been shown to improve the physical stability of the solidified waste, as well as overcoming the inhibiting or set acceleration problems associated with various wastes/39/.

3.2 Cement Additives

Pozzolanic (supplementary cementing materials meeting CAN/CSA A23.5 requirements) and non-pozzolanic mineral additives used in grouts are discussed in the following sections. Table IV identifies some of the various additives used in grouts, and Table A3 (Appendix A) shows some typical chemical compositions for fly ash, slag, and silica fume.

3.2.1 Fly Ash

Fly ash is an industrial by-product produced from the combustion of pulverized coal. Fly ash produced from anthracite or bituminous coals has a low lime content and is pozzolanic. Fly ash produced from sub-bituminous or lignite coals has a high lime content, and can be both cementitious and pozzolanic. Typical properties of fly ash are given in Table A4 (Appendix A). Depending on the lime (CaO) content, ASTM divides the fly ashes into Class F (low-lime, CaO<10%) and Class C (high-lime, CaO>10%). Although replacement levels for fly ash can be as high as 50%/45,H-8/, normally, replacement levels of 10% to 30% are used depending on the pozzolanic activity of the fly ash. The type of fly ash and quantity used will greatly influence the grout mix properties and this must be kept in mind when using this material.

Fly ash mixes tend to hydrate more slowly, which results in reduced heats of hydration/33,45/. This will generally cause a slight increase in the setting time/46,47/ and lower 28-day strengths when compared with equivalent Normal Portland Cement (NPC) mixes/H-8/. After longer curing periods (>90 days), the fly ash mixtures tend to have higher strength than equivalent NPC mixes/45,46,48,49,50,H-8/. Fly ash has been shown to improve the fluidity of cement grouts/47/, and Class C fly ash has been shown to reduce the bleeding to a greater extent than Class F fly ash/12,47,49/. As well, the water requirements for mixes containing Class C fly ash are lower than for mixes containing Class F fly ash/47/. The reduced heat of hydration for fly ash mixes also supports the observation of reduced shrinkage for hardened cement grouts/H-8/; however, for concretes little or no benefit in reducing shrinkage has been observed/47,H-8,H-9/.

The addition of fly ash will, in the long term, result in a denser material with a finer pore structure/51,H-8/. This is due to the secondary reaction of the fly ash with the $Ca(OH)_2$ by-products from cement hydration. The finer pore structure of fly ash grouts explains why lower permeabilities have been observed for these materials/48,52,H-8/. In connection with permeability, some researchers have noted that as the lime content of the fly ash increases so does the permeability of the grout/12,49/. However, some concerns have been raised as to increased rates of carbonation of fly ash grouts/53/.

The wide variety of sources for fly ash has meant a large variability in its chemical composition, and this variability has led to contradictory results from different studies on the observed behaviour of some materials. For example, one source has observed increased expansion for fly ash grout and concrete/50/, while another observed decreased expansion/H-8/. As well, fly ash grout and concrete have been found to have a weaker freeze-thaw resistance; however, it is generally believed that if there is adequate air entrainment (good air-void system) and the concrete is sufficiently aged, then the fly ash has no detrimental effect on freeze-thaw durability/H-10/.

3.2.2 Silica Fume (Condensed Silica Fume)

Silica fume (SF), sometimes referred to as condensed silica fume (CSF), is used as a supplementary cementing material (CAN/CSA A23.5) in cement-based mixtures. SF is a very fine (about 100 times finer than portland cement), very reactive siliceous mineral additive which is a by-product of the silicon metal and the ferrosilicon alloy industries. The chemical analysis of a typical SF is given in Table A3 (Appendix A).

Most experience with SF has dealt with mix contents of about 5% to 20% by weight. An optimum content of 20% was determined in the development of a paste using Sulphate Resistant Portland Cement (SRPC)/52/; however, only a marginal benefit was observed in going from 15% to 20% for a concrete containing SRPC and silica fume/H-11/. It has been observed that the addition of silica fume to a grout will increase the early strength of the grout/40,51,54,55,H-11/. In one case, a 7-day strength increase of 34% was observed with 10% SF replacement/H-11/. The effect of high temperature curing showed that at a curing temperature of 175°C (autoclaved), the early strength decreased, although at a 250°C curing temperature, the early strength again was higher/51/.

The addition of SF has been shown to decrease the porosity and provide a finer pore structure in the grout/48,52/, which in part explains the reduced permeability observed in some cementitious materials/48,51,55,56,H-11/. SF effects on fresh concrete include a reduction of the workability/51,54,H-11/, and an increase of the first peak in the heat output during hydration/54/. SF grouts are thixotropic and exhibit reduced bleeding and segregation relative to normal portland cement grouts/54/. In some cases slight shrinkage increases have been observed with SF grouts/56/. A lower free lime content has been observed with aged grout specimens/56/, which is probably due to the highly pozzolanic nature of silica fume, suggesting that the material should be more durable.

3.2.3 Blast Furnace Slag

Blast furnace slag (BFS) is an industrial by-product produced during the iron smelting process. When quenched from the melt, the slag has a glass-like structure of melilite composition. Its major constituents are silica (SiO_2) and lime (CaO). After the hot slag from the blast furnace is quenched, and dried, it is ground like portland cement. Due to its high calcium content (approx. 40%), BFS is classified as latently hydraulic.

Depending on how finely ground it is, BFS can be used as a partial replacement for cement from 5% to 90%/46,55/. Used in high replacement quantities, BFS can significantly lower the heat of hydration, provide a longer set time, and reduce the creep and shrinkage of a grout or concrete/46/. Used in smaller quantities, BFS has been shown to increase the early strength of grout and concrete/55/, as well as reducing the permeability/52,55,H-7/. One chief disadvantage with the use of BFS is the decrease in workability of the grout mix/49/; however, with the incorporation of a superplasticizer, this can be overcome.

3.2.4 Other Pozzolanic Additives

Many naturally occurring pozzolanic materials were tried in the initial development phase of work carried out at WES/13/. Some of the pozzolans tried include uncalcined diatomite, calcined shale, uncalcined tuff, and pumicite. Note that some of the natural pozzolans are calcined to enhance their pozzolanic activity; this is especially true in the case of clays and shales.

Gypsum-based materials consisting mainly of calcium sulphate hemihydrate have also been added to cement-based mixtures/4,10,50/ in order to enhance pozzolanic activity and to act as an expansive additive.

3.2.5 Non-Pozzolanic Additives

Clays

The addition of clay material to a grout mix is generally for one of two purposes. In connection with grouts developed for use in backfilling, both bentonite and attapulgite have been used/13,26/. The reasons for using these clays were not specifically stated; however, it can be assumed that they were partly used to keep the mix components in suspension, as well as enhancing the expansive characteristics of the grout. Other clays, such as those from the polygorskite (attapulgite) and illite (grundite) clay groups/28,29/ as well as pottery clay/30/ and Conasauga shale/28/, are used in some cases to improve the radionuclide absorption capacity of the grout, and in other instances to help keep the mix constituents in suspension. Ground shale, for example, has been found to reduce the leachability of cesium/6/. In some cases, attapulgite has also been added to reduce the amount of drainable water/28,29/.

Fine Aggregate

Fine aggregate consists of fine to coarse sand, and its use in grouts has both advantages and disadvantages depending on the type and quantity used. Among its advantages are that sand can act as an inexpensive inert filler material while increasing the strength/46,57/, as well as reducing the shrinkage and heat of hydration/57/. However, the disadvantages of using fine aggregate are that it can result in a grout with poor fluid characteristics, making the grout difficult to pump and reducing its working time/H-12/. Although a large variety of sands is suitable for use in cementitious grouts, only those noted in the literature (see Table IV) will be discussed here; these include: dolomite and limestone sand/13,23,46,47/, silica and quartz sand/26,46,49,51,H-13,H-14/, and basalt sand/48/, as well as generic types of

concrete and mortar sands/H-12/. There have also been studies investigating the effect of varying the sand grain size of sand-cement mixes/46,H-12/. In these studies, it was noted that the water/cement ratio had to be increased as the particulate size of the sand was increased, and additionally, finer sands required more cement paste to coat the sand particles due to their relatively large surface area. Silica sand was used in very large quantities (ie, sand/cement >20/1) at Ontario Hydro to develop a relatively strong structural bulk backfill material/H-13,H-14/.

Coarse Aggregates

Various coarse aggregates (anhydrite, dolostone, mudstone, sandstone, halite) combined with grout produced strengths in access of 40 MPa and a permeability less than 10^{-11} m/s/59/. Other work using chert gravel in a grout produced a material with good workability and strengths in excess of 50 MPa/58/. In some mixes, as much as 90% gravel has been used where sealing is not required/59/.

3.3 Chemical Admixtures

Chemical admixtures are used to modify or improve the grout properties for a given application. There are various types available which have been identified in CAN/CSA3-A266.2-M78 Standard. Some of these are briefly described in the following section and are identified in Tables V to IX. Where admixtures are used, the primary and secondary effects should be determined.

3.3.1 Water Reducers/Superplasticizers

A water reducer is an admixture that reduces the amount of mixing water for a given workability/60/. A normal water reducer is capable of reducing water requirements by approximately 10-15%. Superplasticizers, which are a new class of water reducers, can reduce water content up to 30% and can be used to increase temporarily the workability of a grout or concrete mix/H-15/. These admixtures can be used in a grout or concrete mix to increase strength, reduce permeability and porosity, and improve durability. They can also be used to reduce the amount of cement (ie, lower shrinkage and heat development) and increase workability. Table VI lists the references in which specific admixtures are used, and Tables VII and VIII identify some of the commercially available water reducers, retarders (see Section 3.3.2 for retarders) and superplasticizers. The various types of water-reducing admixtures are classified in CAN/CSA-A266.4-M78 and ASTM C-494-81.

Some water-reducing admixtures are more effective when used in mixes containing pozzolans than in plain grout or concrete mixes/61/. In most cases water-reducing admixtures are effective with all types of portland cements, high alumina cements, and sulphate resistant cements; however, some combinations may result in adverse effects, for example, the combination of Type 50 cement with superplasticizers yielded a concrete of very poor durability/H-16/. As well, higher shrinkage was observed with Type 10 than with Type 20 and Type 50 cements relative to the same mixes having no superplasticizer/H-16/.

There have been problems associated with using superplasticizers in conjunction with other admixtures. A grout containing both Mighty-150 (superplasticizer) and Intraplast-N (expanding agent) produced excessive segregation/H-12/, while another grout which contained Melment L-10 superplasticizer in combination with two other admixtures resulted in extended retardation/H-17/. Excessive air contents have been observed with some combinations of admixtures/58/. A melamine-based superplasticizer used in a grout was suspected of causing deterioration of the bond between grout and anhydrite rock, thereby increasing the permeability/24,25/.

Grout and concrete mixtures designed to contain superplasticizers will normally require some adjustment to the mix proportions as outlined in CAN/CSA-A266.5 Standard. An example of a modification required for a concrete containing superplasticizers is the higher "fines" content required to overcome the increased tendency for segregation and bleeding. This problem was observed for one mix containing Mighty 150 and very little "fines"/H-18/.

3.3.2 Set-Retarders

Set-retarding chemical admixtures are used in order to extend the normal working life of fresh grout or concrete. A number of proprietary admixtures are available, a partial list of which is given in reference H-19. The admixtures can be classified as providing normal retardation (Type R), or extended retardation (Type RX). Chemically these are organic salts or acids. Set retarders containing combinations of lignin or carbohydrates and salts of organic acids are classified as water-reducing set-retarding (WR) admixtures and strength-increasing set-retarding (SR) admixtures/H-19/.

Extensive use has not been made of set retarders, despite the requirement of workability for at least 2-3 hours in some cases. They have not been used primarily because some of the superplasticizers or other admixtures used (ie, lignin/62,H-5/) already provide a certain amount of set retardation. In other cases, the mixture contained salt/9,14/ and sugar/28/ which are natural set retarders. The use of set retarders can be restrictive, for example, the time of addition of a set retarder is critical; a delay in adding the retarder after water has been added to the cement can result in increased retardation/4/. This could impose undesirable restraints in the field mixing operations.

Caution should be used when using any admixture, and set retarders are no exception. Among the points to note are the following:

(a) The chemical composition of the cement used may have a significant effect on the retardation/H-19/ (ie, increased retardation with cements having low C_3A content/4/, such as Type 50 and other sulphate resistant cements).

(b) Significant changes in concrete temperature will affect the setting time/H-19/.

(c) The rate and capacity of the plastic concrete to bleed is increased with some types of retarders/H-19/.

(d) Retarders tend to increase the plastic shrinkage, but drying shrinkage is not affected/63/.

(e) Under some conditions, a satisfactory air-void system in the concrete may not be produced/H-19/.

3.3.3 Expanding Admixtures

Three categories of admixtures generally referred to as Expansion-Producing Admixtures are used to offset the effects of shrinkage, both in the plastic and hardened states of grout and concrete. They are as follows:

(a) Admixtures which control settlement and provide expansion in the plastic stage. These admixtures are gas forming or gas generating materials.

(b) Admixtures which control settlement by providing expansion in the plastic and hardened state. These are composed of calcium sulphoaluminate and lime-based materials.

(c) Admixtures which do not control settlement, but provide expansion only in the hardened state. They consist of granulated iron and chemicals that promote oxidation of iron in the presence of moisture and air.

The use of expanding admixtures is important to avoid cracking or poor bond at the grout/host medium interface. Various proprietary expanding admixtures have been studied both within and outside Ontario Hydro. Many of the commercially available expanding admixtures contain chemicals which act as water reducers and/or dispersants, thereby increasing the grout fluidity/H -2,H-20/, and as set retarders/H-21/. When combining admixtures, problems with excessive segregation, or bleeding, may occur/H-12,H-17/. Some admixtures may have detrimental effects on other grout properties such as reduction in the compressive strength and increasing the air content/H-12/.

Natural expansive additives have been used that react with the cement hydration by-products to form expansive cement components. Calcium sulphate, which reacts with the tricalcium aluminate (C_3A) portion of the cement to form the expansive component ettringite/4/, has been added to some grouts/15,22/. Likewise, calcium chloride/26/ forms expansive compounds (including Friedels salt) generated by the reaction between the chloride and alkali-reactive aggregates/4/. Magnesium oxide (MgO) was found to accelerate the formation of tobermorite gel, and it also generally causes expansion by formation of brucite ($Mg(OH)_2$)/51/. Other expansive admixtures used in grouts are included in Table VI.

3.3.4 Other Admixtures

There are a variety of other admixtures which are used to produce special modifications in a grout mix/H-5,H-12/. These have been identified in ACI Committee 212 Report No. IR-81. These admixtures include flocculants, thickening agents, defoamers and pumping aids (Table IX). As with other admixtures, they may have secondary effects on the grout and concrete properties, which should be investigated.

4.0 GROUTS REVIEWED

Pumpable cement-based grouts developed in the U.S. for use in plugging boreholes and filling shafts are discussed. Selected U.S. developed grouts are given in chronological order in Table X. These grouts, although not specifically developed for near-surface applications, may have property requirements that are needed for the LLW and MLW program at Ontario Hydro. A considerable amount of research has also been conducted at other institutions, including Ontario Hydro. The information reviewed has been identified according to where the grouts were developed.

4.1 U.S. Waterways Experiment Station (WES)/SANDIA Work

Since 1975, both WES and Sandia Laboratories have been working on the development of pumpable, durable cement-based, expansive grouts for use in plugging boreholes. Based on this work, five grout mixtures were chosen for further study (Table B1 - Appendix B). Field trials were also carried out using similar grouts (Tables B2 and B3 - Appendix B), and long-term durability studies on a few formulations are in progress/2,3,19/. Table X gives a chronological outline of the work carried out at both laboratories.

Grouts tested at WES were made using different types of hydraulic cements including some portland cements, sulphate resistant cements, expansive cements, and shrinkage-compensating/expansive cements. Some grouts contained no pozzolans and others contained varying amounts of different pozzolans (usually fly ash). Chemical admixtures were used to lower the water/cement ratio, to reduce the permeability and porosity, and to increase the density, strength and durability/2,4/. Expansive additives were included in several grouts to maintain contact with the host media.

Extensive testing has shown that phase composition and microstructure are common to most grouts, and that despite a wide range of starting grout compositions, most grouts tend toward a uniform phase composition with time. The many grouts studied show a wide range of physical characteristics, but in most cases the properties tend to be as good as or better than the tentative requirements given in Table II.

Durability studies of 2, 3 and 4 year old grouts/3,19,26/ indicate that the grout mixes developed have maintained acceptable physical properties with time. The compressive strength for all grouts have shown a one year strength at least 50% greater than the 28-day strength, and the values for the dynamic modulus seem to increase for a year before stabilizing.

Water permeability of the grout BCT-IFF was less than 10^{-11} m/s after 4 years for field and laboratory specimens/19/. It was observed that simulated borehole (SBH) specimens/11,43/ were unsuitable for measuring the permeability of the grout-to-rock interface because of a tendency to crack due to the radial stresses imposed upon the host medium by the expansive grout. Cracking of the grout along the grout/rock interface due to drying shrinkage is also a problem with SBH's. These problems have resulted in inconsistent and excessive permeabilities being measured with SBH specimens. Excessive permeabilities have also been measured due to dissolution of the grout at the grout/host medium interface/24,25/.

Expansion of the moist cured grout BCT-IFF shows that all specimens had a net positive expansion at 1 year/19/. Other grouts developed including field samples have exhibited surface cracking (generally less than 1 mm in width). The cracking is believed to be primarily caused by volume change of the grout due to changes in moisture content, temperature, continued hydration, or a combination of these.

Quality control procedures should be followed during field mixing and placement of the grout, to ensure that there are no detrimental effects on the grout properties. It was also noted that a 17-year old grout sample obtained from a mine plug/20/ was in good condition, despite the fact that the grout had a relatively low strength and a high water/cement ratio.

4.2 Pennsylvania State University (PSU) Work

Development work began at PSU in the late 1970's. Most of the research has centered on developing expansive grout formulations/4/, which have been classified according to the type of expansion/25/.

A variety of cements have been tried at PSU, but the most widely used cement is a sulphate resistant Class H. High-lime and low-lime fly ash, as well as silica fume, has been added as pozzolanic material. A wide range of chemical admixtures, including superplasticizers, defoamers, and expansive agents, has also been tried. The concern with the expansion mechanism of grouts has also led to the use of a variety of natural expansive additives. Among the expansive additives tried are Gypseal (calcium sulphate), sodium chloride, and calcium chloride. A summary of selected PSU mix formulations is given in Table B4 - Appendix B.

Although a common set of variables was not studied for many of the mixes developed, some trends in material behaviour have emerged. The use of a low w/c ratio is of primary importance for achieving adequate properties for the grout, since lowering of w/c ratio almost always increases the compressive strength. A reduction in the permeability is realized with the use of plasticizers (water reducers) due to the corresponding decrease in the w/c ratio. In addition, the permeability has also been found to be reduced with the inclusion of pozzolanic materials such as silica fume and high-lime fly ash in the mix. The effect of high temperature on some grout properties has been studied/64/, and although it is not of particular concern to the LLW and MLW study, some researchers believe that high temperature studies could be used to simulate longevity effects.

The expansion of grouts is based on different mechanisms and can be significantly affected by curing conditions. In some grout mixtures, expansion via the formation of mineral ettringite has been well documented/4,65,66,67/. Two expansive stages are usually observed. In the first, hemihydrate reacts to form gypsum, accompanied by initial rapid formation of ettringite. At this point the paste is still plastic and the net expansion is minimal. The second stage causes the expansion of hardened cement paste through slow reaction between sulphate in the pore solution and the constant supply of aluminate. For 28 to 90 days after mixing, second-stage expansion is a function of the calcium sulphate content. Although the

storage environment for LLW and MLW waste will not be saline, it has been identified that grouts made with saturated salt brine or large quantities of NaCl will expand by different, more complex, mechanisms. Friedels salt, which forms by the reaction between chlorides and C_3A, is the main expansive component, with secondary mechanisms contributing to the overall expansion.

4.3 Other Grouts

A few preliminary grouts were developed at Ontario Hydro for use in the LLW and MLW studies/H-22/. The required mix properties were a flowable/pumpable grout with minimal shrinkage and a permeability in the order of 10^{-12} to 10^{-14} m/sec. The mix components consisted of readily available materials, such as portland cement (Type 10), concrete sand, a superplasticizer, and an expanding/water reducing admixture. Based on six trial grouts (see Table B8 - Appendix B) two mix formulations were chosen for further study, which provide a compressive strength in excess of 50 MPa, as well as having a permeability in the order of 2×10^{-13} m/s at 150 days of age (Table B9 - Appendix B). Permeabilities of the rock-grout interface were also measured, and these values were of the same order of magnitude as for the grout samples alone.

A limited investigation on the fresh properties of several high-density grouts was carried out at Ontario Hydro/H-17/. The mix components consist of Type 10 cement, fly ash, specularite sand, and four different admixtures (Table B5 - Appendix B). Water to (cement + fly ash) ratios ranging from 0.4 to 0.54 were tested, and aggregate-to-cement ratios of 3.5/1.0 and 1.5/1.0 were tried. Highly flowable grouts with 28-day strengths ranging from 18 MPa to 52 MPa were developed; however, no tests were done for other properties.

Other grout studies carried out at Ontario Hydro included using ordinary portland, sulphate resistant (API-Class G), and aluminous cements, combined with fly ash and blast-furnace slag to develop grouts with strengths ranging from about 30 MPa to 70 MPa. Permeability values of less than 10^{-11} m/s were obtained (see Table B6 - Appendix B).

A British study on the use of ordinary portland cement (OPC) with sand, fly ash, and blast-furnace slag developed highly flowable grouts with strengths in excess of 30 MPa, and it identified the typical additive/cement ratios, flow rates, working times, and heat development values (see Table B7 - Appendix B).

5.0 BULK BACKFILL CEMENTITIOUS MATERIALS

5.1 Sand-Cement Mixes

Various sand-cement grouts using a variety of sand types and water/cement ratios have been studied/46,H-12/. It has been observed that changing the sand-cement ratios and sand type can modify the physical characteristics of grouts significantly. It is necessary to use the correct aggregate grading to avoid pumping problems such as segregation/46,H-12/, and it has been recommended that for long pumping distances a maximum particle size of 1 mm be used/46/. The segregation problem has been found to be minimal for both masonry and concrete sand mortars when the water/cement ratio is less than 0.45/H-12/ (see Figure C1 - Appendix C). The use of a thixotropic admixture was also found to reduce segregation/H-12/. For many sand-cement grouts, the

workability is retained only for a short period of time (5-30 min); however this problem could be alleviated with the use of plasticizers/H-12/. As the particle size of the sand is decreased, the water requirement is increased in order to maintain the same workability. Strength of sand-cement grouts can vary from 20 MPa to 50 MPa at 7 days depending on the amount of cement, sand type and water/cement ratio (see Figures C1 and C2 - Appendix C). No test results were available on the permeability measurements, or hardened grout shrinkage/expansion.

Large quantities of sand mixed with 2 to 8 percent by weight of cement have been used in bulk backfill applications/H-8,H-9/. The backfill consisted of lean grout mixes (containing sand, cement, and water) and a material referred to as controlled density backfill (containing sand, cement, fly ash, and water). The mix proportions of both materials are given in Table C1 - Appendix C. These mixes were intended to provide better physical characteristics than common backfilling materials, and were designed to develop strengths of 700 kPa and a 3500 kPa.

Another structural backfill material was developed using cement contents from 2 to 4 percent by weight/H-14/. Two types of mixes were developed, a slurry mix, to which water was added, and a "dry" mix for which the natural moisture content of the sand in the range of 10-20 percent was used to provide water for the cement hydration. Although the water content in the mixes was low, the water/cement ratios were quite high, varying from 5 to 25, because the cement quantity added is also very low. Both clean sand and sand contaminated with silt and clay were tested in order to represent possible field conditions, and it was found that the addition of contaminating materials had no adverse effect. It was noted that even moderate compaction of the placed material improved significantly the compressive strength of the cemented backfills mixed at their natural moisture content. The results for these mixes indicate that adequate strength for backfill purposes can be achieved, with a compressive strength as high as 900 kPa in some cases/H-19/. The cemented backfill would be self supporting in excavations, and on steep slopes. There were some problems with excessive shrinkage of the slurry mixes; however, no quantitative measurements were made. Permeability tests were also done on 50 x 100 mm cylinders in a triaxial cell. The permeabilities were found to be 1.5×10^{-6} and 7.4×10^{-7} m/sec for mixes with 2 and 4% cement, respectively.

6.0 SUMMARY

Based on the literature reviewed, conclusions on various aspects of the state of grout development for use in the disposal of radioactive wastes can be made.

The following items are among those which indicate the progress of the work to date:

(1) Grout-design technology has advanced to the point that future materials research can proceed along a narrower field of study that takes into account site-specific characteristics.

(2) The influence of the individual mix components on the grout properties is reasonably well understood, and it has been shown that almost all grout properties can be modified by the use of the proper mix components in correct proportions.

(3) All grouts for use in the disposal of radioactive wastes should be non-shrinking or expansive to some extent. The mechanisms and factors affecting grout expansion are well understood.

(4) The sorptivity of cement-based materials for a variety of radionuclides has been established; however, waste-specific radionuclides need to be investigated.

The literature also identified areas of study which require additional work. Among the areas, in which questions still remain, are the following:

(1) The longevity and chemical stability characteristics of most grouts have yet to be determined.

(2) Potential problems associated with emplacement characteristics such as pumpability, feasibility, effect of emplacement on material properties, and quality control have not been adequately addressed.

(3) The thermal expansion and contraction characteristics for most of the materials reviewed have not been established.

(4) Problems related to the shrinkage of a grout due to excessive heat of hydration have not been considered.

(5) The shrinkage/expansion and permeability characteristics of sand-cement grouts have not been adequately studied.

Some of the tentative requirements to achieve a durable grout have been identified in the literature as follows:

(1) Low water/cement ratios must be used to achieve adequate strength and to minimize porosity and permeability.

(2) The use of properly graded aggregates is important to achieve the required pumpability, as well as avoiding segregation problems.

(3) The use of fly ash or slag as supplementary cementing material is necessary in order to (a) reduce the cement content (thereby lowering the heat of hydration and reducing the chance of drying shrinkage cracks), and (b) enhance the durability of the grout.

(4) The use of admixtures (ie, superplasticizers) will reduce the w/c ratios while maintaining a workable grout for ease of placement.

(5) If the grouts are to be subjected to aggressive ground water attack, then low tricalcium aluminate (C_3A) content and sulphate resistant cements should be considered for use.

7.0 RECOMMENDATIONS

Based on the literature reviewed, a small number of basic mix components are indicated for use in the development of a grout for low-level and medium-level radioactive waste storage applications. These mix components and the advantages and disadvantages associated with the use of each are highlighted in Table XI. In order to address questions regarding the durability/stability of potential materials, experimental work should be initiated.

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TABLE I

Engineering Properties of Interest for Cementitious Materials

Mechanical	Hydraulic	Chemical	Thermal	Emplacement
Compressive strength	Permeability	Leachability	Expansion/ contraction	Working time
Tensile strength		Sorptivity	Conductivity/ diffusivity	Bleeding and Segregation
Bond		Longevity/ stability	Heat of hydration	Fluidity/Pumpability
Longevity				Feasibility of emplacement methods
Ductility/Elasticity				Effect of emplacement on seal properties
Shrinkage/Expansion				Quality control

TABLE II

Tentative Grout & Concrete Properties
Recommended for the Disposal of Radioactive Wastes Underground

Property	Recommended Concrete Properties(a)	Recommended Grout Properties(b)
Density, g/cm^3	-	-
Unconfined Compressive Strength, MPa	40-50	>24
Young's Modulus (dynamic GPa)	45	>14
Unrestrained Volumetric Expansion, %	0.2-0.3	-
Interface Permeability, m/s	-	-
Permeability, m/s	10^{-11}	$<10^{-12}$(c)
Push-out strength, MPa	-	-
Viscosity/Workability	-	<100 poises at 3 hours
Other		(d)

(a) - Reference 4
(b) - Reference 7
(c) - at three months
(d) - the grout should have physical and chemical compatibility with the host medium

TABLE III

Various Cements Encountered in Literature

Cement Type	References	
Portland cements:	External	Ontario Hydro (H-)
Type 10	6,29,42,47, 54	5,7,12,16,17,20,21, 22,24,25
Type 20	6	16
Type 30	6,13	5,25
Type 40		12
Type 50		11,16
Sulphate Resistant:		
Class C (API Classification)	12,14,26,37, 49,62	
Class G (API Classification)		7,11
Class H (API Classification)	4,10,12,14, 15,37,48,49,50, 51,62	
Type K (ASTM Classification)	2,9,13,14,37	
High Alumina Cement		12
Slag Cement	42	
Masonry Cement	30,35,39	

TABLE IV

Additives Encountered in Literature

Pozzolanic	References		Non-Pozzolanic	References	
	External	Ontario Hydro (H-)		External	Ontario Hydro (H-)
Natural Pozzolans:			Clays:		
uncalcined diatomite	13		bentonite	13,26,48	
calcined shale	13		attapulgite	26,28,29,30	
uncalcined tuff	13		illite (Grundite)	28,29	
pumicite	13		pottery clay	28,30	
calcium sulphate hemihydrate	4,10,50		shale	6,28	
slaked lime	39				
ground limestone	39				
Fly Ashes:			Fine Aggregates:		
Class C (CaO>10%)	2,3,10,12,13,26,47,50,64		dolomite & limestone sand	13,46,47	
(high lime)	4,22,49		silica & quartz sand	10,26,51,62	13,14
(lignite)	49	26	basalt sand	48	
			salt	4	
Class F (CaO<10%)	12,37,46,47,48,50		silica flour	10	
(low lime)	4,45,53		baselite sand	13	
(bituminous)	49	7			
(Kingston FA)	28,30,49		Coarse Aggregates:		
(Appalachian FA)	62		anhydrite	4,22,58	
(Lakeview FA)		27	dolostone		
			mudstone		
Blast Furnace Slag	46,48,51,53,62	7	sandstone		
			halite		
Silica Fume (Condensed)	4,48,50,51,54 55,56	11	chert gravel	57	
			unspecified gravel	58	23

TABLE V

Chemical Admixture Categorization

Type of Admixture	Purpose	Remarks
Air-Entraining	To improve durability	Entrains air in the form of minute bubbles distributed evenly throughout concrete. Also increases workability.
Water-Reducing	To reduce water required for a given consistency or increase slump for a given water content.	Some water-reducing admixtures may also retard setting time of concrete. Some may also entrain air.
Retarding	To retard setting time of concrete.	Use where delayed setting and hardening required, eg., hot weather, extended placing times.
Accelerating	To accelerate setting time and strength development of concrete.	Not an antifreeze. Calcium chloride most common accelerator but is not generally recommended.

TABLE VI

Admixtures

Type	Reference	
	External	Ontario Hydro (H-)
Water Reducers/ Superplasticizers:		
Sulphonated melamine condensate	24,25,26,54	
(Melment L-10)	13	11,16,18,22,25
Sulphonated napthalene condensate -	51	
(Lomar D)*		18
(Mighty 150)	4	12,16,17
Modified Lignosulphates		
(Mulcoplast CF)		16
CSA Type WN		27
25XL		12,23
Melgram 1	10	
Melgram 2	10	
Lignin		5
Set Retarders:		
See Reference H-10 for more details		
Plastiment	13,26	

Type	Reference	
	External	Ontario Hydro (H-)
Expanding admixtures:		
Propiretary -		
Interplast C		21
Sternson's Grout Aid		20
ASGA		20
Interplast N		5,12,17,20
Intrusion Aid		17,20,22
Other -		
Aluminum powder		5,20
Calcium sulphate	4,15,22	
Calcium chloride	4,26	
Magnesium oxide	51	
Ferrosilicon dust	4,62	
Dehydrated ludox	62	
Dehydrated silic acid	62	
Other admixtures:		
Flocculant -		
Conbex 653		12
Conbex 209X, Polyox, K15H		5
Hydroxyethyl Cellulose		28
De-Foamer -		
Nopco NX2, De Air No. 1	13	
not specified	23,26,37,62	

*Could also be considered a modified lignosulphate

TABLE VII

Commercial Water Reducers and Retarders

Brand Name	Supplier	Active Ingredient	Effects	Dosage* (ml/kg)	Specific Gravity (g/ml)
Admix 42	MAC	Synthetically modified lignosulphonate + formate	Water reduction and set acceleration 0.5-2 hr.	5-20	1.15
Admix 132D	MAC	Refined lignosulphonate	Water reduction 10-15% and set retardation 2-3 hr	2.4	1.16
Daratard-40	W.R. Grace	Lignosulphonate	Water reduction up to 15% and set-retardation 2-4 hr.	4-8	1.15-1.20
Mulcoplast 20	Mulco Inc.	Synthetically modified lignosulphonate	Water reduction	5	1.14-1.16
Paric 1	Fujisawa	Salt of hydrocarboxylic acid	Water reduction	2	1.10
Plastiment	Sika Chemical Corporation	Salt of hydrocarboxylic acid	Water reduction retardation	1.3-2.6	-
Plastocrete	Sika Chemical Corporation	Salt of hydrocarboxylic acid	Water reduction	1.3-2.6	-
Porzite L-932	Sternson Ltd	Hydroxycarboxylic acid + molasses	Water reduction up to 10% and 2 1/2-3 hr. retardation	1.25-1.20	1.20

TABLE VII (Cont'd)

Commercial Water Reducers and Retarders

Brand Name	Supplier	Active Ingredient	Effects	Dosage* (ml/kg)	Specific Gravity (g/ml)
Porzite L-70	Sternson Ltd.	Lignosulphonate + formate	Higher than 10% and normal set	4	1.20
Pozzolith 100N	Master Builders	Hydroxylated polymers	Water reduction	1.25-1.20	1.23
Pozzolith 100R	Master Builders	Hydroxylated polymers	Water reduction and retardation	2.4	1.15
Prokrete L-70	Protex Ind	Lignosulphonate	Water reduction up to 10%	1.3-2.6	1.22
Prokrete R	Protex Ind	Lignosulphonate + hydroxycarboxylic acid	Water reduction up to 10% and retardation 1-2 hr.		
WRDA	W.R. Grace	Lignosulphonate	Water reduction up to 15%	4-5	
Admix 105 XR	Modern Advanced Concrete	Hydroxycarboxylic acid	Set retardation 2-4 hr and water reduction 4-8%	2-4	1.12
Daratard H.C.	W.R. Grace	Hydroxycarboxylic acid	Set retardation 2-3 hr and water retardation 5-10%	1.2-2.6	1.20

TABLE VII (Cont'd)

Commercial Water Reducers and Retarders

Brand Name	Supplier	Active Ingredient	Effects	Dosage* (ml/kg)	Specific Gravity (g/ml)
H.C. Retarder	Sternson Ltd.	Hydroxycarboxylic acid	Set retardation 3-9 hr. and water reduction	2-3	1.24
Paric T	Fujisawa	Hydroxycarboxylic acid	Set retardation and water reduction	2-3	1.17
Pozzolith 100 XR	Master Builders	Hydroxylated polymer	Set retardation 1 hr. and water reduction	2-3	1.22
Sodium Heptonate	Croda Chemicals	Sodium Heptonate	Retardation 5-9 hr. and water reduction	1-2	1.27

*Unless otherwise stated

TABLE VIII

Commercial Superplasticizers

Brand Name	Manufacturer or Supplier	Form	Active Ingredient	Effects	Dosage (by wt. of cement)	Specific Gravity	Shelf Life
PSP-R	Protex Industries	Liquid	Modified Naphthalene Sulphonate	Water reduction 25% Retardation 1-3 hr.	5-20 ml/kg	1.205	1 yr.
PSP-N	Protex Industries	Liquid	Modified Naphthalene Sulphonate	Water reduction up to 25%	5-20 ml/kg	1.200	1 yr.
Mighty 150	ICI Americas Inc.	Liquid	42% aq. soln. of high mol. wt. of sulpho-aryl alkylene + carboxylic-acid salt	Water reduction 15-20% + set retardation	0.6-1.2%	1.20	-
Mulcoplast CF	Mulco Inc.	Liquid	Sulphonated polymer	Water reduction up to 25%	7.55-20 ml/kg	1.07-1.09	>1 yr.
Sikament	Sika Chemical Corp.	Liquid	Anionic Dispersant	Water reduction up to 30%	7.8-23.4 ml/kg	1.2	>1 yr.
Melment - L10	Sternson Ltd.	Liquid	Sulphonated Melamine	Water reduction up to 30%	1.5-3.0%	1.11	>1 yr.
Melment - F10	Sternson Ltd.	Solid	Sulphonated Melamine	Water reduction up to 30%	0.3-0.6%	-	>1 yr.

TABLE IX

Materials Commonly Used as Flocculating Agents

Product Name	Manufacturer	Chemical Identity	Physical Characteristics	Effects in Cement/Water System	Product Application
Natrosol	Hercules Inc U.S.	hydroxy ethylcellulose	fine white powder soluble in hot and cold water	increases viscosity of water phase	thickener suspending agent, water retainer
Carbopol 801	B.F. Goodrich Canadian	polyacrylic acid polymer	powder soluble in water and polar solvents	increases viscosity of water phase	thickener, increases cohesion
Methocel F	Dow Chemical U.S.	hydroxy propyl-methylcellulose	powder treated for dispersible in water, solubility pH controlled	increases viscosity of water, mix thixotropy	thickener, suspending
Methocel A	Dow Chemical U.S.	methylcellulose	water-dispersible powder	increases viscosity and	thickener, water retainer
Modocol E	Modo-Chemie Sweden	hydroethylmethyl	fine powder, soluble in water	increases viscosity and thixotropy of mix	thickener, bonding agent
Polyox WSR 301	Union Carbide U.S.	polyethylene oxide polymer	slowly dissovling in water, solubility increased by addition of isopropanol	increases both viscosity and thixotrophy; stringy mix at higher dosages	thixotropic agent, flow agent
Alginates	Alginates Ind. U.K.	natural water-soluble gum from brown seaweed (alginic acid)	powder, water-soluble dependent on di-valent ion (CA^{2+}) concentration and rate of shear	increases viscosity and mix lubricity	thickener, workability aid
Calgon	Calgon Corp U.S.	polyacrylamide	water-soluble	flocculation; increases viscosity by bridging cement particles	thickener for reducing bleeding

TABLE IX (Cont'd)

Materials Commonly Used as Flocculating Agents

Product Name	Manufacturer	Chemical Identity	Physical Characteristics	Effects in Cement/Water System	Product Application
Separan	Dow Chemical U.S.	sulfated polysaccharide	slowly dissolving in water	increase viscosity of water phase	water retainer
Acrysol ASE 75	Rohm & Haas Co. U.S.	natural salt of acrylic acid polymer	water-dispersible solid	increases viscosity of water	thickener, workability aid
Krilium	Monsanto Chem Australia	CA^{2+} salt of vinyl acetate maleic anhydride co-polymer	powder, soluble in water	increases thixotropy effect, increasing alkali content of cement	increase cohesion of mix, reduces bleeding capacity
Stymer S	Monsanto Chem U.S.	Na^{+} salt of styrene-maleic anhydride co-polymer	soluble in cold water	increases viscosity of water phase	thickener suspending aid
Silica fume	Elborg Technology Co.	fumed silica	insoluble in water	shear thinning thixotropic agent	increase cohesion of mix, improve pumpability
Aerosil	Degusa U.S.	finely divided silica	insoluble in water	viscosity increased	improve bleeding characteristics
Volclay		bentonite	insoluble in water	viscosity increased	improve bleeding characteristics

TABLE X

Selected Borehole Sealing Development Work in the U.S.

Author	Reference Number	Source	Report Date	Comments
J.A. Boa, Jr.	13	WES	1978	- 100 preliminary mixes - 59 mixes studied in some detail - 5 mixes selected for further testing
C.W. Gulick, Jr.	14	SAND	1978	- 1 year results for 5 mixes selected above/2/ (BPN-FA-SP-P, BPN-CS-FA-1, BPN-FA-BS-SP-P-1, BP-521-25MP, BPN-FA-BS-SP-P-1)
C.W. Gulick, Jr.	34	SAND	1979	- development of mixes for plugging ERDA-10 borehole - Plugs 1,2,3 & 4
C.W. Gulick, Jr. J.A. Boa, Jr. D.M. Walley A.D. Buck	26	SAND	1979	- 2 year durability studies of 5 mixes (BP...) - study of effect of different cement types on 5 grouts
C.W. Gulick, Jr. J.A. Boa, Jr. A.D. Buck	9	SAND	1980	- development grouts for Bell Canyon Test (BCT) (DHT-1, DHT-2, DHT-3 and 24 variations of the first 3) - final choice of BCT-IF (salt water grout) & BCT-IFF (non-salt grout) - field places mixes based on BCT-IFF called Plug ONE (9/26/79) and Plug ONEX (2/14/80)
C.W. Gulick, Jr. J.A. Boa A.D. Buck	2	SAND/ WES	1981	- 4 year durability study of 5 original mixes - 2 and 3 year durability study of ERDA 10 plugs and Plugs ONE & ONEX
A.D. Buck K. Mather	3	WES	1982	- durability studies similar to those in reference 2 above

TABLE X (Contd)

Selected Borehole Sealing Development Work in the U.S.

Author	Reference Number	Source	Report Date	Comments
D.M. Roy M.W. Grutzeck K. Mather A.D. Buck	15	PSU/ WES	1982	- joint effort between PSU & WES on grout development (PSU designation 80-081) to study reproducability of results at different laboratories
D.M. Roy F.L. Burns	22	PSU/ ONWI	1982	- detail two mixes (79-091, 80-081) developed in earlier report (#6)
A.D. Buck, etal	37	WES	1983	- detail 8 variations of BCT-IFF grout - 4 different cement and various additives were tested
D.M. Roy M.W. Grutzeck L.P. Wakeley	4	PSU	1985	- detailed coverage of grout development work to date at PSU, WES, DOWELL and SANDIA
M.W. Grutzeck D.M. Roy	64	PSU	1985	- cover briefly PSU work in grout development - detail mixes 83-03, 83-06 - consider effect of curing time, temperature and pressure
A.D. Buck	10	WES	1985	- development of sanded BCT-IFF grout (called TT84) for use at Terra Tek test site
L.D. Wakeley D.M. Walley A.D. Buck	19	WES	1986	- 5 year and 3 year durability studies of field placed grouts grouts SPDV and B-25

TABLE XI

Basic Mix Components Recommended for use in LLW and MLW Grout Development

Materials	Advantages	Disadvantages
Cements:		
Portland Type 10	- readily available - behaviour is well understood	- may not provide all the desired material behaviour characteristics
Portland Type 50	- sulphate resistant - low heat of evolution	- may behave unsatisfactorily when combined with certain chemical admixtures
Type K (Shrinkage Compensating)	- provides positive expansion force against host medium walls - prevents shrinkage cracking	- may not be readily available
Additives:		
Fly Ash (Class F and Class C)	- reduces heat of hydration - increases setting time - improves fluidity of fresh grout - hardened material has a finer pore structure and therefore reduced permeability - may reduce bleeding - may reduce shrinkage	- lower 28-day strengths - the finer pore structure may be detrimental to the freeze-thaw durability
Silica Fume	- decreases porosity of hardened material in the long-term, leading to a reduced permeability - higher early strength	- reduces the workability of the fresh grout - increases heat of hydration

TABLE XI (Cont'd)

Basic Mix Components Recommended for use in LLW and MLW Grout Development

Materials	Advantages	Disadvantages
Additives: (Contd)		
Blast Furnace Slag	in large replacement quantities: - lower heat of hydration - increases setting time - reduces creep and shrinkage in small replacement quantities: - may increase early strength - may reduce permeability	- workability of fresh grout is reduced
Plaster (Calcium Sulphate Hemihydrate)	- enhances the pozzolanic activity, thereby creating a finer pore structure and reduced permeability - acts as an expansive additive	- may reduce freeze-thaw durability
Sand	- grading and type could improve grout strength - reduced shrinkage - lower heat of hydration - helps in the sorption of cesium and carbon	- grading and type can affect pumpability - can increase water demand - can reduce workability time - improper mix design could result in segregation problems
Admixtures:		
Superplasticizers	- can increase fluidity of grout - can reduce water requirements	- some superplasticizers used along with Type 50 cement can result in a low durability grout - may increase segregation - care must be used when combining several admixtures

TABLE XI (Cont'd)

Basic Mix Components Recommended for use in LLW and MLW Grout Development

Materials	Advantages	Disadvantages
Admixtures: (Contd)		
Expansion Admixtures	-can provide a positive expanding force if required -some admixtures can also act as water reducers	-must use great care in combining with other admixtures (ie, Mighty 150 and Intraplast N resulted in excessive egation)
Thixotropic Admixtures	-may be useful in reducing segregation problems associated with pumping of sanded grouts	-may affect other grout properties

APPENDIX A

Individual Mix Components

APPENDIX A - LIST OF TABLES

	TITLE
Table A1	PHYSICAL PROPERTIES AND CHEMICAL COMPOSITION OF PORTLAND CEMENTS
Table A2	PROPERTIES OF VARIOUS GROUTS
Table A3	PROPERTIES OF SUPPLEMENTARY CEMENTING MATERIALS
Table A4	TYPICAL PROPERTIES OF FLY ASHES

TABLE A1

Physical Properties and Chemical Composition of Portland Cements (Typical Results of Ontario Cements)-1980

	Type 10[1]	Type 20[2]	Type 30[4]	Type 40[3]	Type 50[4]
Loss on Ignition %	0.63 to 1.93	1.0 to 2.1	1.0	0.88 to 1.59	1.0
Insoluble Residue %	0.03 to 0.3	0.2 to 0.3	0.11	0.35 (one test)	0.16
SiO_2 %	19.7 to 22.1	21.6 to 22.3	21.1	22.2 to 22.6	23.03
Al_2O_3 %	3.5 to 6.3	4.5 to 5.6	4.6	4.6 to 5.20	3.20
Fe_2O_3 %	1.9 to 3.2	4.0 to 4.8	1.7	4.4 to 5.30	3.71
CaO	62.5 to 63.7	59.9 to 62.3	63.2	60.7 to 62.1	63.95
MgO %	1.9 to 3.9	2.4 to 2.7	3.7	2.4 to 2.6	2.81
SO_3 %	2.4 to 3.7	2.0 to 2.8	3.8	2.1 to 2.4	1.89
C_3S %	40.7 to 52.4	31.0 to 47.0	52.4	28.1 to 39.8	51.7
C_2S %	18.6 to 29.5	27.5 to 46.3	21.0	33.7 to 43.1	26.7
C_3A %	6.3 to 13.0	41. to 7.6	9.4	4.0 to 6.0	2.2
C_4AF %	7.4 to 9.1	12.2 to 14.6	5.1	13.3 to 16.2	11.3
Na_2O equiv %	0.95 to 1.3	0.76 to 1.0	0.81	0.85 to 1.03	-
Blain cm^2 g	3394 to 3789	3260 to 3600	5590	2989 to 3388	3560
Set time h:m	1:40 to 2:00	2:25 to 3:59	0.45	3:06 to 3:52	2:15
Air %	-	7.1 to 8.9	-	-	-
Soundness %	-	0.0 to 0.06	0.34	0.00 to 0.04	-
Strength psi					
1	-	825 to 1275	3245	-	-
3	2780 to 3560	1450 to 2460	4270	1210 to 1800	2422
7	3530 to 4100	2430 to 3450	-	1711 to 2750	3260
28	4580 to 5110	4610 to 5400	5895	3680 to 5290	4900
90	-	-	-	6230 to 6775	-
Heat of Hydration (7 d) cal/g	-	66.1 to 70.1	-	64.8	-

(1) Range of results of 4 plants in Ontario. One sample at random from each plant.

(2) Range of results (14 tests) of one plant at random over two year period.

(3) Range of results (8 tests) of one plant at random over one year.

(4) One sample at random from a plant.

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TABLE A2

PROPERTIES OF VARIOUS CEMENTS

Property	Oil Well Class G Cement*	Low Heat Portland Cement	High Alumina Cement	Sulphate Resistant Portland Cement	Chemstress Type K
Cl. No.	69747	-	49749	70146	WES#RC749
Symbol	API-G	LHPC	HAC	SRPC	-
Chemical Composition: (wt percent)					
CaO	63.76	62.7	37.21	62.82	55
SiO_2	22.82	23.9	5.04	22.46	15.5
Al_2O_2	2.85	3.84	37.58	2.79	9.2
MgO	3.23	1.98	1.26	3.27	1.4
Fe_2O_3	3.83	3.70	15.93	3.92	2.1
So_3	1.95	2.35	0.14	2.03	15.3
K_2O	0.38	0.69	0.11	0.41	0.32
Na_2O	0.39	0.22	0.04	0.45	0.34
TiO_2	0.15	-	1.5	0.17	-
P_2O_5	0.05	0.10	0.06	0.06	-
Mn_2O_3	0.07	-	0.03	0.08	-
SrO	0.03	-	0.02	0.04	-
ZnO	0.01	-	0.02	0.01	-
LOI**	1.19	0.82	2.74	0.91	1.6
Insol. Res.	0.10	-	1.0	0.20	-
$\underline{Cl}$	0.0040	-	0.0049	-	-
F	0.0027	-	0.0016	-	-
Compounds:***					
C_3S	54.5	39.8	-	51.6	-
C_2S	24.3	38.5	-	26.2	-
C_3A	1.6	2.3	-	1.4	-
C_4AF	11.7	11.3	-	11.9	-
Physical Properties:					
Rel. Density	3.17	3.21		-	-
Blaine Fineness (m^2/kg)	310	360		-	-

(CV10)

* This API Class G cement also meets CSA Type 50 sulphate resistant portland cement requirements.

** Loss on Ignition at 950°C

*** Cement chemical notation: C = CaO, S = SiO_2, A = Al_2O_3 and F = Fe_2O_3

TABLE A3

PROPERTIES OF SUPPLEMENTARY CEMENTING MATERIALS

CEMENTING MATERIAL SYMBOL	CLASS C FLY ASH FA	CLASS F FLY ASH FA	BLAST FURNACE SLAG BFS	CONDENSED SILICA FUME SF
OXIDES (%):				
CaO	29.9	2.8	38.16	0.17
SiO_2	32.7	42.3	37.89	92.7
Al_2O_3	16.7	23.2	8.39	0.17
MgO	5.6	0.96	11.55	0.59
Fe_2O_3	6.4	14.7	(1.42 AS Fe)	0.29
SO_3	2.9	0.87	(2.01 AS S)	0.36
K_2O	0.36	2.1	0.47	0.95
Na_2O	1.22	0.66	0.17	0.16
P_2O_5	1.04	0.49	<0.01	0.06
LOI	0.4	7.96	-	3.24
RELATIVE DENSITY	2.70	2.31	2.94	2.22
BLAINE (m^2/kg)	413	381	410	6000

(CV10)

TABLE A4

TYPICAL PROPERTIES OF FLY ASHES

Type of Coal Source for Each Fly Ash	Chemical Analysis (percent)									
	SO_2	Al_2O_3	Fe_2O_3	S+A+F	Free CaO	Total CaO	MgO	SO_3	Alkalies as Na_2O	Loss on Ignition
Bituminous Blend	46.1	19.0	18.6	83.7	2.2	8.2	1.3	1.6	0.72	2.0
Lignite	37.1	11.8	7.3	56.3	0.5	21.8	5.6	2.6	4.23	0.3
Subbituminous	28.8	20.0	4.1	53.0	2.1	32.0	6.4	3.8	0.66	0.2
Subbituminous	51.8	27.2	2.0	81.0	1.9	10.7	2.1	0.7	0.86	1.2
Lignite	31.1	17.1	7.9	56.1	0	25.3	8.1	3.3	1.35	1.1

Type of Coal Source for Each Fly Ash	Physical Analysis						
	Specific Gravity	Autoclave Expansion (percent)	Specific Surface (cm^2/cm^3)	Percent of Control 28 days	Strength Lime-Pozzolan 7 days (lb/in^2)*	Increase in Flow	Reactivity Alkalies 14-day (percent)
Bituminous Blend	2.44	- 0.004	7 413	81.8	957	27.0	45.4
Lignite	2.69	0.0110	4 729	56.6	781	33.0	42.0
Subbituminous	2.72	0.116	12 835	90.7	517	38.0	18.0
Subbituminous	2.32	0.038	3 805	93.6	155	32.0	48.5
Lignite	2.71	0.070	12 834	79.1	808	32.0	46.2

* 1 lb/in^2 = 6.895 kPa

APPENDIX B

Grouts Reviewed

APPENDIX B - LIST OF TABLES

	Title	Reference Source
Table B1	MIX PROPORTIONS OF BELL CANYON TEST (BCT) DEVELOPMENT GROUTS	2
Table B2	MIX PROPORTIONS OF FIELD PLACED GROUTS RELATED TO BCT DEVELOPED GROUTS	19
Table B3	MIX PROPORTIONS OF BCT-IFF (NON-SALT) GROUT	2
Table B4	VARIOUS PSU FORMULATIONS	4,64
Table B5	MIX PROPORTIONS AND PROPERTIES OF SOME HIGH-DENSITY GROUTS	H-17
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TABLE B1

MIX PROPORTIONS OF BELL CANYON TEST (BCT) DEVELOPMENT GROUTS

	Proportions (w/o)				
	BPN-FA-SP-P	BPN-FA-BS-SP-P-1	BPN-CS-FA-1	BPN-521-25MP	BPN-FA-BS-SP-P-1(TYIII)
Cement, Type III	-	-	-	-	46.6
ChemComp Cement	51.9	46.6	50.7	38.5	-
ChemStress Cement	-	-	7.3	7.9	-
Fly Ash	17.5	15.7	13.7	11.0	15.7
Tufa (pozzolan)	-	-	-	8.7	-
Fine Salt	-	9.6	-	-	9.6
Melment (L10)	1.4	1.2	1.4	1.9	1.3
Plastiment	0.1	0.1	0.1	0.1	0.1
Water	29.1	26.8	26.7	31.9	26.7
Properties					
Water-to-Cementitious Material, Ratio	0.42	0.43	0.37	0.48	0.43
Fluid Density, g/cm^3	1.89	1.90	1.96	1.81	1.90
Fluid Density, lb/ft^3	117.8	118.6	122.4	113.0	118.6
Fluid Density, lb/gal	15.7	15.9	16.4	15.1	15.9

(CV10)

TABLE B2

MIX PROPORTIONS OF FIELD PLACED GROUTS RELATED TO BCT DEVELOPED GROUTS

Grout	Mass Used Per Cubic Foot of Grout Made, lb			
	BCT-1FF	BCT-1FF	SPDV	B-25
Component:				
Class H cement	69.82	69.68	73.73	70.31
Fly ash	23.76	23.71	24.65	23.79
$Ca(SO)_4$	8.50	8.48	4.93	8.99
Dispersant	0.925	1.12	0.73	1.06
Defoamer	0.02	0.02	0.02	0.20
Water	8.33	27.81	27.89	25.78
TOTAL	131.36	130.82	131.95	129.13
Fluid density: lbs/gal	17.6	17.5	17.6	17.4
Ratio of water to cementitious solids, by mass	0.28	0.27	0.27	0.25

(CV10)

TABLE B3

MIX PROPORTIONS OF BCT-1FF (NON-SALT) GROUT

	Proportions (w/o)		
	Lab	Plug One 09/26/79	Plug Onex 02/14/80
Added Material			
Class H Cement	52.20	53.1	52.7
Fly Ash	17.6	18.1	18.2
Expansive Additive	7.0	7.1	7.5
Dispersant (D65)	0.2	0.1	0.2
Defoamer (D47)	0.02	0.02	0.02
Water	23.0	21.6	21.4
Properties			
Water-to-Cementitious Material Ratio (by weight)	0.30	0.276	0.273
Fluid Density (g/cm^3)	1.98	2.11	2.11

(CV10)

TABLE B4

VARIOUS PSU FORMULATIONS

COMPONENTS	FORMULATION* (PARTS BY WEIGHT OF CEMENTITIOUS SOLIDS)									
	SALT							NON-SALT		
	BCT-IF	80-081** (PSU/WES)	81-081**	81-03**	82-14	83-03	83-05	BCT-IFF	82-03	83-06
Class H Cement	67.95	68.00	68.48	69.08	60.00	68.55	60.28	67.95	60.22	60.27
Condensed silica Fume	-		15.76	-	10.00	-	-	-	6.04	-
Silica Flour	-	-		-	-	-	12.37	-	6.13	12.36
High-lime fly ash	22.96	22.90	-	-	15.00	23.08	20.24	22.96	19.36	20.25
Low-lime fly ash	-		11.55	11.34	15.00	-	-	-	-	-
Ferrosilicon Dust	-		-	15.46	-	-	-	-	-	-
$CaSO_4$ 1/2 H_2O (Expansive Additive)	9.04	8.34	4.2	4.12	-	8.37	7.11	9.09	8.25	7.12
NaCl	8.86	4.05	4.08	4.01	11.57	8.97	11.79	-	-	-
Quartz Sand (graded to C109)	-	-	-	-	-	200	-	-	-	-
20 X 40 Sand	-	-	-	-	-	-	31.08	-	-	31.08
D30 Sand	-	-	-	-	-	-	31.08	-	-	31.08
ASTM C109 Sand	-	-	49.24	49.31	110	-	-	-	-	-
Superplasticizer	0.27	1.1	1.0	1.36	1.0	3.34	1.33	0.27	1.43	1.99
Defoamer	0.02	0.02	-	-	-	0.23	0.21	0	0.02	0.22
Water	30.00	29.4	30	29.89	28.12	27.82	31.72	25.07	25.40	32.22
W/C[1]	0.44	0.43	0.44	0.43	0.47	0.41	0.53	0.37	0.42	0.53
W/S[2]	0.30	0.30	0.30	0.30	0.28	0.28	0.32	0.25	0.25	0.32
W/SCS[3]	0.27	0.28	0.29	0.28	0.25	0.25	0.28	0.25	0.25	0.32

(CV10)

* From reference 64 unless otherwise noted
** From reference 4
1. Water/cement ratio
2. Water/cementitious solids (first seven ingredients in table) ratio
3. Water/total solids ratio

TABLE B5

MIX PROPORTIONS AND PROPERTIES OF SOME HIGH-DENSITY GROUTS

MIX IDENTIFICATION	TYPE 40 CEMENT g	FLY ASH g	ADMIXTURE (g)				SPECULARITE SAND g	GROSS W/C+F	FRESH MIX PROPERTIES				COMPRESSIVE STRENGTH MPa 50 mm CUBES		
			1	2	3	4			FLOW CONE (secs) 13 mm ORIFICE OPENING	EXPANSION %	BLEEDING %	DENSITY kg/m^3	1	2	28
12390	1600	-	12	32	-	-	5800	0.45	43	-	-	3023	No Cubes Made		
12391	1600	-	12	32	-	-	5800	0.40	>60	4.0	Trace	-	12.1	17.2	19.4
12392	1440	160	12	32	-	-	5800	0.45	>60	3.0	0.5	2052	18.4	25.9	32.8
12395	1600	-	12	32	-	-	5800	0.42	-	-	-	2910	11.7	17.1	18.2
12397	1440	160	12	32	-	-	5800	0.40	>60	4.0	Trace	2934	8.5	20.5	24.2
13300	1600	-	12	24	4.6	-	5800	0.47	37	-	-	2800	13.4	17.2	20.2
13301	1600	-	12	32	4.6	-	5800	0.44	41	-	-	-	16.8	20.3	25.1
13304	1600	-	-	-	-	-	4000	0.45	30	-	2.0	3110	24.1	46.7	51.7
13305	1600	-	12	-	-	-	4000	0.43	52	1.2	2.4	3025	17.2	34.0	40.6
13306	1440	160	12	-	-	-	4000	0.44	63	1.5	1.5	3000	15.7	32.1	40.7
13307	1440	160	12	16	-	-	4000	0.40	53	-	1.0	2940	9.6	27.5	35.3
13308	1600	-	-	-	-	8	4000	0.54	21	1.9	3.4	2895	No Cubes Made		

(CV10)

TABLE B6

PROPORTIONS OF GROUTS MADE WITH THREE DIFFERENT CEMENT TYPES

(approx. 130 days water curing at 7°C)

GROUT	W/C (Constant Flow)	AVERAGE APPARENT POROSITY (%)	AVERAGE COMPRESSIVE STRENGTH (MPa)	WATER PERME-ABILITY ($m/s \times 10^{-11}$)	AVERAGE BULK DENSITY kg/m^3
1. API-G	0.393	25.7	72.8	0.5	2035
2. API-G + FA	0.471	36.1	39.2	22.	1852
3. API-G + BFS	0.450	30.7	50.7	1.1	1925
4. NPC	0.471	31.3	52.0	< 0.13	1884
5. NPC + FA	0.550	39.6	28.7	73.	1785
6. NPC + BFS	0.493	31.8	48.5	0.4	1857
7. HAC	0.436	36.4	50.3	1.5	2071
8. HAC + FA	0.486	42.4	38.1	140.	1895
9. HAC + BFS	0.379	33.5	66.7	1.2	2087

TABLE B7

PROPORTIONS OF SAND OR BFS OR FLY ASH (PFA)/CEMENT GROUTS

Additive	Typical Additive/ Cement Ratio	Particle Size Range and Shape	*Flow and Pumping Properties	Critical Range of Water/Solids	Working time (Setting)	Strength and Strength Development	Centre drum temperature 220 dm^3 drum
SAND	1:1 to 3:1	0.1-0.5 mm depends on grading table irregular	*Depends on sand grading Poor modified by plasticisers Particle size distribution critical	0.4-0.6 depends on sand	short 5-25 mins increased by retarders	20N-50N/mm^2	3:1 Sand/OPC 60°C
PFA	1:1 to 10:1	0.01-0.001 mm round	easily pumped over wide range, modified by plasticisers	0.3-0.6	1-5 hrs	3N-20N/mm^2 depends on PFA/cement ratio; early strength low	3:1 PFA/OPC 60°C
BFS	1:2 to 9:1	0.01-0.1 irregular	easily pumped, modified by plasticisers	0.3-0.45	1-5 hrs	10-50N/mm^2 early strength low	9:1 BFS/OPC 60°C
CLAYS		< 0.005	easily pumpable, plasticisers have little effect	0.5-2.0	10-30 mins	very low ~1N/mm^2	-

Flow characteristics (standard flow tests)	Flow table	Colcrete test
3:1 Sand/OPC (W/C = 0.56)	105	(too stiff)
3:1 PFA/OPC (W/S = 0.42)	(too fluid)	400 mm

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TABLE B8

GROUTS DEVELOPED AT ONTARIO HYDRO - MIX PROPORTIONS AND TEST RESULTS

Mix Identification	GROUT PROPORTIONS (g)					W/C Ratio	FLOW[3]		Density (kg/m^3)	COMPRESSIVE STRENGTH (MPa)		
	Lab Standard Type 10	Concrete Sand[1]	Admixture		Water[2]		Horizontal mm	Vertical mm		Age (Days)		
			Intrusion Aid	Melment L10						1	7	28
13579	8800	13200	-	-	3520	0.40	185	108	2286	25.0	50.5	64.2
13580	22000	-	-	-	7700	0.35	215	140	2048	31.0	57.1	67.5
13581	8800	13200	88	-	3520	0.40	210	135	2162	15.8	38.6	50.5
13582	22000	-	220	-	7700	0.35	300	150	-	-	-	-
13583	8800	13200	-	132	3520	0.41	325	150	2277	17.9	49.2	60.5
13584	22000	-	-	330	7440	0.35	390	150	2071	23.4	60.7	74.7

(CV10)

[1] Fineness Modulus : 2.75
[2] Water absorption of sand satisfied
[3] 75 x 150 mm Cylinder

TABLE B9

PERMEABILITY OF GROUTS DEVELOPED AT ONTARIO HYDRO

Identification	Permeability m/s									
	Age (Days)									
	10	20	23	38	43	49	55	90	120	150
13579	-	-	-	-	-	2.95×10^{-12}	-	-	-	2.11×10^{-13}
13580	-	-	-	-	-	-	2.0×10^{-13}	1.75×10^{-13}	-	-
13581	-	1.5×10^{-12}	-	3.16×10^{-13}	-	-	-	-	-	2.61×10^{-13}
13582	-	-	-	-	-	2.4×10^{-12}	-	-	1.6×10^{-13}	-
13583	1.64×10^{-12}	-	-	-	4.8×10^{-13}	-	-	1.28×10^{-13}	-	-
13584	-	-	-	-	-	-	3.3×10^{-13}	-	-	-
Rock Core/1/	3.9×10^{-13}	-	-	-	-	-	-	-	-	-
Rock Core in Grout Mix #13583	-	-	5.7×10^{-13}	-	-	-	-	1.89×10^{-13}	-	-
Shelby Tube in Grout Mix #13583	-	-	4.79×10^{-13}	-	-	-	-	-	-	-

/1/Core is taken from UN-2 (a 243 m deep borehole on the Darlington GS property) from depth 31.55 - 31.80 m along incline of borehole.

APPENDIX C

Bulk Backfill Cementitious Materials

APPENDIX C - LIST OF TABLES/FIGURES

	Title	Reference Source
Table C1	MIX PROPORTIONS FOR STRUCTURAL BACKFILL MATERIALS	H-13
Figure C1	PROPERTIES OF GROUT AT DIFFERENT W/C RATIOS - 1.5:1 SAND/CEMENT	H-12
Figure C2	PROPERTIES OF GROUT AT DIFFERENT W/C RATIOS - 3:1 SAND/CEMENT	H-12

TABLE C1

MIX PROPORTIONS FOR STRUCTURAL BACKFILL MATERIALS

	K-Krete		Lean Mix	
	700 kPa	3 500 kPa	700 kPa	3 500 kPa
Cement	40.5*	70	82	161
F.A.	121.5	210	-	-
Sand **	1,654	1,607	1,653	1,640
Water **	305	275	345	330
Per Cent Cement	2	3.2	4	7.6

* Quantities shown are in kg/m^3.
** The final quantities of sand and water are to be determined from the flow test. However, the values indicated are very close to final ones and could be used as a guide for the first flow test.

(CV10)

1.5:1 SAND/CEMENT GROUTS

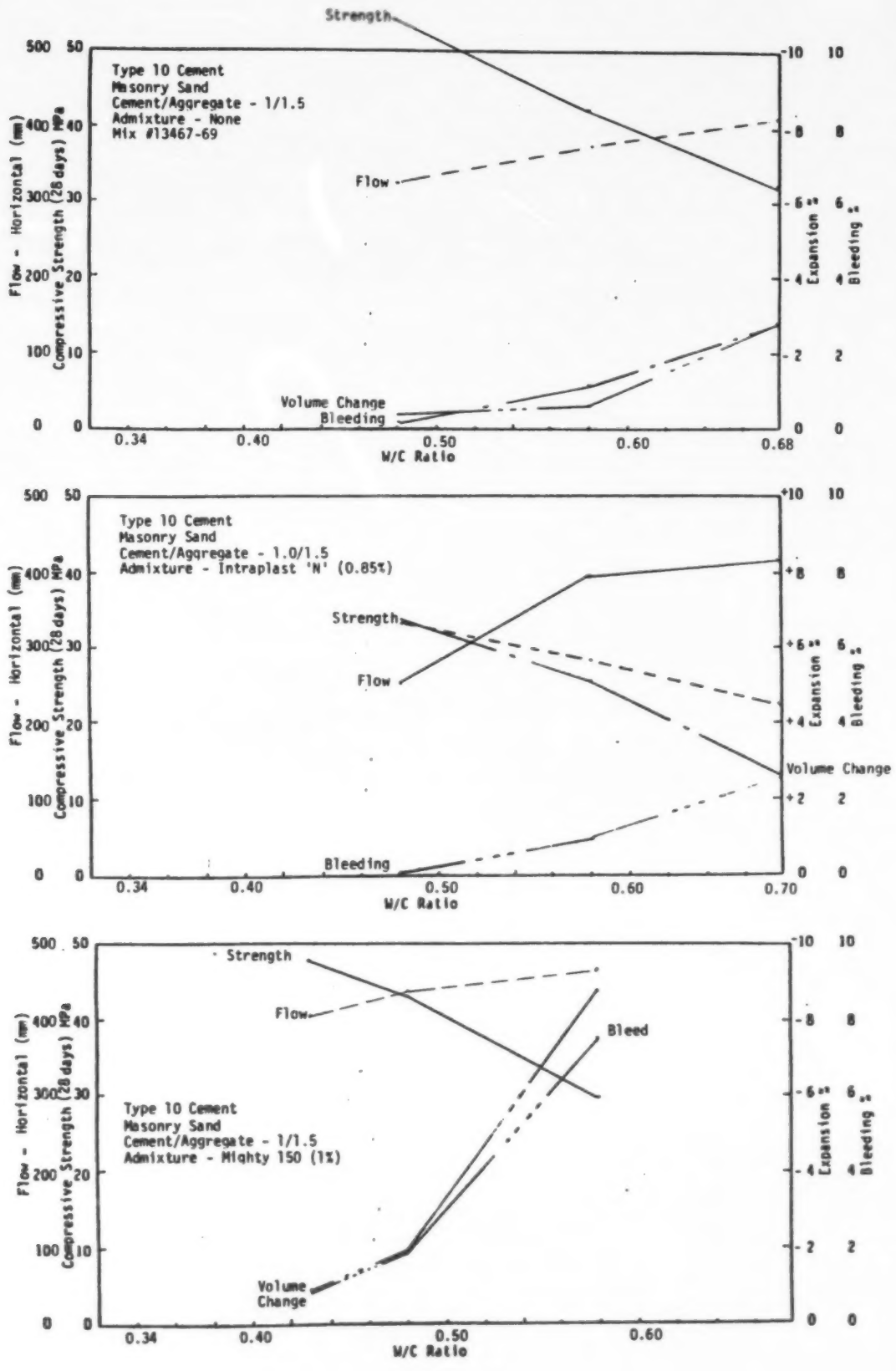

FIGURE C1
PROPERTIES OF GROUT AT DIFFERENT W/C RATIOS

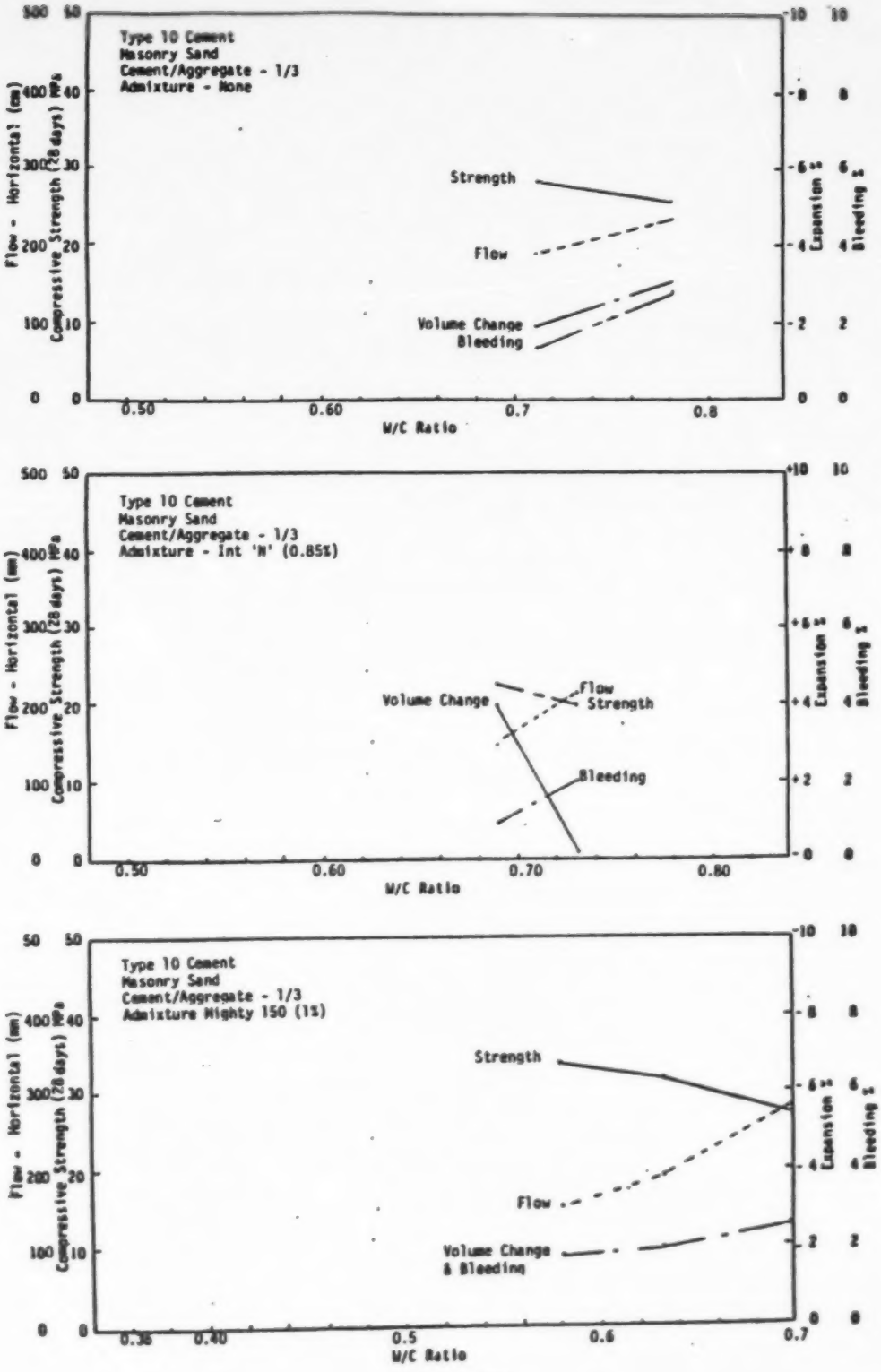

FIGURE C2

PROPERTIES OF GROUT AT DIFFERENT W/C RATIOS

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